Assessment of Premature Creep Failure by Degradation of Microstructures in Advances High Cr Ferritic Steels (先進高Crフェライト鋼における早期クリープ破壊の組織劣化に基づく評価)

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論文内容要旨

Since a main source of CO_2 emission in the world is the combustion of oil, coal, and natural gas in the fossil fired power plants, the improvement of energy efficiency is one of the most important requirements in electrical power generation. Process control measures such as reducing the amount of excess air are able to contribute to increased thermodynamic efficiency but the most significant increases may only be obtained by increasing the live steam temperature.

To achieve this goal, development of new materials with high oxidation resistance and creep strength are key issues. High Cr ferritic steels with the lower cost, smaller coefficient of thermal expansion (CTE) and higher thermal conductivity as compared to austenitic stainless steels are being extensively used in power plants in Japan. Cr is the basic alloying element for high Cr ferritic steels, and increased Cr content to 9-12% Cr improves oxidation and corrosion resistance. But, unexpected premature creep failure of 9-12% Cr heat resistant steels due to overestimation of long-term creep rupture life has been recently reported. This study mainly focused on 4 topics. First, the causes of overestimation and prevention of the overestimation by multiregion analysis have been discussed. Second, the hardness drop of aged materials without stress in long-term region is proposed for detection of premature creep failure. In order to have a good understanding about the causes of the loss of strengthening mechanisms and the consequent hardness drop and premature creep failure, in third topic the recovery of dislocation substructures and in forth topic the coarsening and disappearance of particles have been studied. The conclusions are summarized as follows.

1. Assessment of Premature Creep Failure in Advanced High Cr Ferritic Steels

Creep rupture life during the long-term service is evaluated from short-term experimental data with the aid of Time-Temperature-Parameter (TTP) methods. Orr-Sherby-Dorn (OSD) method is a representative one in the case of creep rupture. The basic assumption of conventional TTP methods like Orr-Sherby-Dorn

is the constant temperature dependence of t_r (Q_a) for creep rupture data in both short-term and long-term creep regions. Creep rupture data of 7 kinds of high Cr feritic steels with different Cr and W concentration have been analyzed by Orr-Sherby-Dorn method. The following results are obtained.

1. Creep rupture data of steels containing less than 8% Cr are characterized well with unique apparent activation energy and these steels do not show premature creep failure in long-term creep region.
2. In advanced high Cr ferritic steels containing more than 8% Cr the apparent activation energy for rupture life sometimes changes from a high value of short term creep to a low value of long term creep. This change results in overestimation of rupture and is called "Premature Creep failure". In order to avoid overestimation of creep rupture life in long-term region, it is necessary that a set of creep rupture data be divided into several data sets so that activation energy is unique in each data set. This method is called "Multiregion analysis". Multiregion analysis represents well and without overestimation creep rupture life of 9-12% Cr steels in long-term creep region.
3. The increase of activation energy results in increase of creep rupture life. In the high stress and short-term region, creep rupture life increases up to 9%Cr with increasing activation energy. The increase of rupture life continues at $C_{Cr} > 9\%$ with increasing Cr concentration despite the constant activation energy. In the low stress and long-term region characterized by the low activation energy in steels containing more than 9% Cr, creep rupture life decreases with increasing Cr concentration, because activation energy decreases with increasing Cr concentration in this region.

2. Detection of Premature Creep Failure by Hardness Measurement of Aged Materials without Stress

As safe operation of power plants becomes a serious problem we should be able to detect the boundary of decrease in activation energy and the consequent transition of premature creep failure. In the present study, the hardness measurement of aged microstructures without stress has been proposed. The results reported in literature exhibit that the hardness of aged microstructures under stress in gauge portions usually decreases during creep. The reduction of hardness during creep is not only due to thermally activated degradation mechanisms at high temperature exposure but also may be due to creep plastic deformation. But the decrease in hardness of aged microstructures without stress is just influenced by thermally activated mechanisms. Hardness of aged microstructures without stress in grip portions of crept samples were measured for the whole steels studied and the obtained results are as follows.

1. In steels without premature creep failure the hardness of aged microstructures decreases continuously with increasing exposure time.

2. In 9-12% Cr steels with premature creep failure hardness of aged microstructures remains almost constant during aging for short duration, whereas it decreases with increasing time after long term aging. There is a good accordance between the onset of the hardness drop and the decrease in activation energy.
3. The hardness drop can be a good measure of the onset of premature creep failure and the decrease in activation energy.
4. It is evident that degradation of microstructure and the consequent softening is the main cause of unexpected breakdown of creep rupture life in long term creep region.

3. Recovery of Dislocation Substructures

In order to have a good understanding about the constant hardness in short term and the hardness drop in long term region we need to consider microstructural degradations and strengthening mechanisms which can take place during high temperature exposure. Subgrains size of aged microstructures during high temperature exposure without stress and microstructural changes during creep have been evaluated in both short-term region characterized by the high activation energy (Q_H) and long-term region characterized by the low activation energy (Q_H). The results summarized as follows:

1. In steels without premature creep failure the early onset of reduction in hardness of aged microstructures without stress can be attributed to the early onset of recovery of dislocation substructure.
2. In steels with premature creep failure, dislocation substructure of aged microstructures without stress is stable in short-term region and after a certain time of aging, recovery of dislocation substructure occurs in long-term region. The constant hardness of aged microstructures without stress can be attributed to stable dislocation substructure and the considerable recovery of dislocation substructure in long term region brings about the softening of microstructure and the consequent hardness drop.
3. Steel containing 9% Cr has the lowest recovery rate and the latest onset of recovery of dislocation substructure in long-term region.

4. Coarsening and Disappearance of Precipitates

The dispersed precipitates within subgrains and on the subgrain boundaries pin the mobile free dislocations and sub-boundaries. $M_{23}C_6$, MX and partially M_2X particles precipitate during tempering, while Fe_2 (W, Mo) Laves phase, Z phase and M_6C particles form during exposing at creep temperature. $M_{23}C_6$ and MX particles have the lowest inter particle spacing after tempering and hence these precipitates play a major role for pining of mobile free dislocations and sub-boundaries. However, loss of precipitation hardening due to coarsening and/or disappearance of particles may occur during high temperature exposure. The obtained results in this topic are summarized as follows:

1. In short-term region, the stable dislocation substructure can be attributed to the constant interspace of $M_{23}C_6$ particles that act as pining points for the motion of free dislocations and subgrain boundaries. Whereas, the considerable increase in interspacing of $M_{23}C_6$ particles results in significant recovery of dislocation substructure in long-term region.
2. The addition of Cr from 9 to 12% accelerates the coarsening rate of $M_{23}C_6$ and Laves phase particles.
3. Steel containing 9% Cr has the lowest rate of coarsening and disappearance of particles during long-term exposure and as a consequence displays the highest creep strength in long-term creep region.

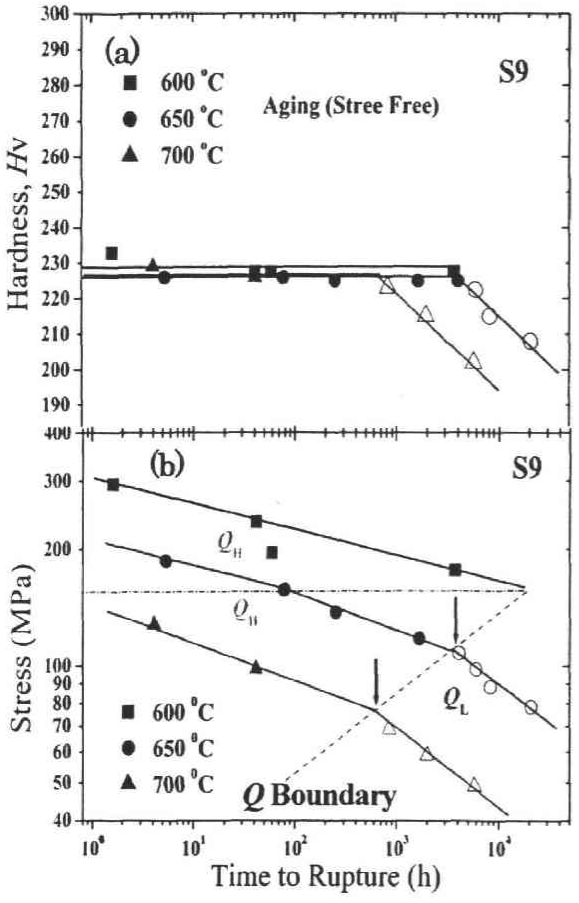


Figure 1 (a) Vickers hardness measured in a grip portion and (b) creep rupture data of steel S9. Downward arrows indicate the onset of hardness drop at each temperature.

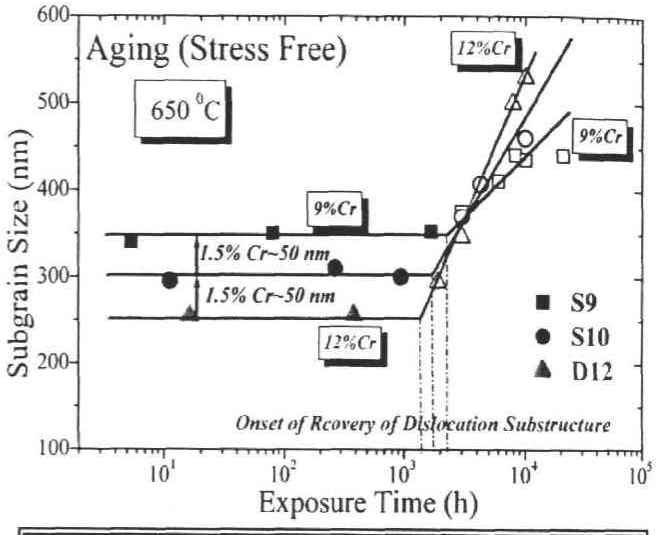
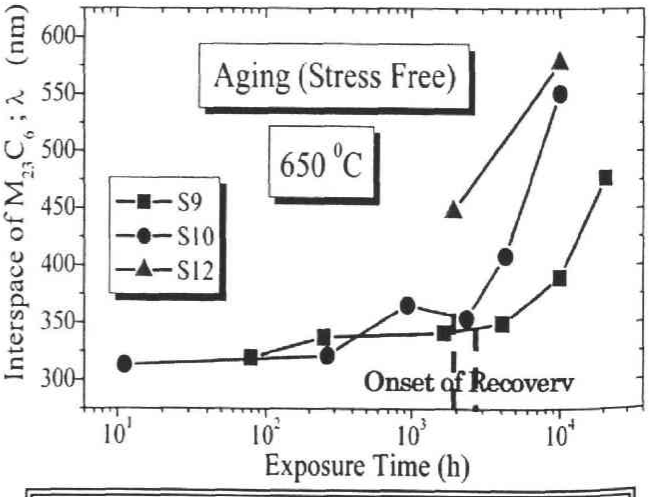


Figure 2. Interspaces of $M_{23}C_6$ particles as a function of aging time without stress at 650 °C for steels S9, S10 and D12.



Figures 3. Subgrain size of aged materials without stress as a function of exposure time at 650 °C. Down arrows show the onset of premature creep failure.

論文審査結果の要旨

火力発電プラントでは，高 Cr フェライト鋼が数多く使われている。この種の耐熱鋼では，長時間使用後に，急激な強度低下(早期破壊)が起きる可能性がある。日本の蒸気火力発電プラントの80%は，設計寿命を越えて使われており，これらの経年プラントでは，安全確保のために，早期破壊の予知と防止が，重大な関心事である。このような背景のもとに，本論文では，高 Cr フェライト系耐熱鋼の早期クリープ破壊の機構を明らかにし，それを予知する指針を得ることを目的とした。論文は全 8 章で構成されている。

第 1 章は序論であり，本研究の背景が述べられている。

第 2 章は目的であり，研究の目的と論文の構成が述べられている。

第 3 章は実験方法であり，使用した材料，クリープ試験，組織観察の方法等が述べられている。

第 4 章では，5～12%Cr を含むフェライト鋼について，そのクリープ破断時間を領域区分法に基づいて解析した。その結果，材料が使われる長時間側には，破断時間の活性化エネルギーの小さい領域が出現し，このことが長時間挙動を過大評価する原因であることを明らかにした。

第 5 章では，活性化エネルギーの小さい領域の出現を非破壊試験で予知する方法論について検討した。その結果，無負荷部での，回復にともなう硬度低下と，活性化エネルギーの低下がよく対応することを見出した。

第6章では，無負荷部でのラス組織の回復挙動および，クリープ変形中のラス組織の回復・劣化挙動について詳細に検討した。その結果，ラス組織の時間依存型回復の開始が，活性化エネルギーの低下および無負荷部での硬度低下の原因であることを明らかにした。また，ラス組織の回復速度はクロム濃度に依存することを示した。

第7章では，各種炭化物や窒化物，金属間化合物などの析出物がクリープ中に析出，凝集粗大化する挙動や，析出物の組成変化を詳しく検討した。その結果，$M_{23}C_6$ 型の炭化物が最も密に析出していること，この析出物の凝集がラス組織の安定性を支配していることを明らかにした。また，ラス組織の安定性がクロム濃度で変化することは，析出物凝集速度のクロム濃度依存性に起因することを示した。

第8章は結論であり，本研究の成果を総括している。

以上要するに，本論文は， 高 Cr フェライト系耐熱鋼の早期クリープ破壊の機構を明らかにし，それを予知する方法論を提案したもので，材料システム工学の発展に寄与するところが少なくない。

よって，本論文は博士（工学）の学位論文として合格と認める。